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(71) Applicant: BASF AG, Ludwigshafen

(72) Inventors: *see original document*

(54) Supported catalysts for the production of ethylene oxide

Patent Claim

Catalysts for the production of ethylene oxide from ethylene and oxygen based on  $\alpha$ - $\text{Al}_2\text{O}_3$  as the support material and silver as the active mass, characterised by the fact that the catalysts' content of alkali-soluble Si compounds is below 0.001 wt-% calculated as  $\text{SiO}_2$  and relative to the total weight of the catalyst.

Supported catalysts for the production of ethylene oxide

The present invention relates to improved supported catalysts for the production of ethylene oxide from ethylene and oxygen.

The conversion of ethylene and oxygen to ethylene oxide using silver-containing supported catalysts is generally known. The catalysts which are suitable for this reaction and the numerous modifications as regards their chemical composition, physical properties and method of preparation are also well-known from the patent literature and the rest of the technical literature so it is unnecessary to set out the prior art in detail.

In general these catalysts contain as their principal active constituent ca 2-12 wt-% of metallic silver, relative to their total weight, plus various modifying agents - principally alkali-metal compounds - in smaller amounts as promoters, which basically produce an increase in selectivity, ie raise the yield of ethylene oxide per unit of oxygen reacting.

Support materials proposed up to now include clay, bauxite, kieselguhr, graphite, pumice and aluminium oxide. Although strictly speaking a support material is inert towards the catalysed reaction it is nevertheless frequently not without influence on the properties of the catalyst, either by activating or deactivating it or in relation to its mechanical properties. For these reasons  $\alpha$ - $\text{Al}_2\text{O}_3$  has up to now proved particularly beneficial as a support material.

Nevertheless catalysts of this kind leave something to be desired in so far as the thoroughly satisfactory activities and selectivities achievable with them cannot be maintained at their original level over long periods of operation.

The aim of the invention was therefore to deal with this drawback.

It has been found that with such supported catalysts suitable for the production of ethylene oxide from ethylene and oxygen based on  $\alpha$ - $\text{Al}_2\text{O}_3$  as the support material and silver as the active mass particularly long operating periods without large activity or selectivity penalties can be achieved if their content of alkali-soluble Si compounds is below 0.001 wt-% calculated as  $\text{SiO}_2$  and relative to the total weight of the catalysts.

From DE-OS<sup>1</sup> 19 36 233 catalyst supports for the catalysts in question are known which contain 1-6 wt-% of SiO<sub>2</sub> in addition to aluminium oxide but this document gives no indication of the effect of the SiO<sub>2</sub>, let alone of its adverse properties.

By "alkaline Si compounds" is meant compounds which dissolve in an excess of 0.1 N NaOH within 10 mins at 100°C. Only Si compounds of this kind have, according to observations to date, an adverse effect on the catalyst properties, and by contrast poorly soluble silicates, for example, are harmless.

The catalysts in accordance with the invention are prepared using Si-free chemicals to produce the active mass and as the carrier material a correspondingly pure  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. If  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> of this quality is not obtainable commercially one starts with normal commercial  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, boils it for 30 mins with an approximately equal quantity of 1 wt-% NaOH, and then washes it with totally deionised water until the moist  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> has a pH below 8.  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> treated in this way generally contains less than 0.0001 wt-% (= 1 ppm) of alkali-soluble Si compounds, measured as SiO<sub>2</sub>.

In a similar way the content of alkali-soluble Si compounds in commercial  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> can be reduced below 1 ppm SiO<sub>2</sub> if it is boiled for 10 mins with approximately the same quantity of 1 wt-% hydrofluoric acid and then washed with water until the moist  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> has a pH greater than 5.

The content of alkaline Si compounds can be determined by the method described in the *Handbuch der analytischen Chemie*, Vol IV a  $\alpha$ , pp 505 ff, Springer-Verlag, 1967: a 20 g sample of the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> to be investigated is boiled for 10 mins with 20 ml 0.1 N NaOH and the Si in the NaOH solution is determined photometrically as molybdatosilicic acid.

The support material is generally used in the form of sintered shapes such as spheres, rings and tablets 3-15 mm in diameter.

To produce the catalysts ready for use the pre-treated  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> support is impregnated as usual with a solution which contains the desired quantity of silver as silver nitrate and in addition as appropriate the nitrates of promoter metals such as Li, Na, K, Rb, Cs and/or Ba, the quantity of liquid being equal to the absorptive capacity of the support. In doing this it is possible to use adjuvants such as amines in the normal way. The impregnated mass is then dried in the convection oven at 220°C until all the silver has been deposited on the support in metallic form.

Frequently such a catalyst is subsequently treated with an additional promoter to increase the selectivity. Most such catalysts fall under the following general definition:

ca 88 - 98     wt-%  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>  
ca 2 - 12     wt-% Ag  
0 - 0.035 wt-% Li, Na and/or K  
0 - 0.025 wt-% Cs (applied in a subsequent treatment)

As regards the promoters the ones mentioned here are only the examples which are preferred in industry. In principle the catalysts can also contain other or additional promoters because according to observations to date the beneficial effect in accordance with the invention is always to be expected when the content of alkali-soluble Si compounds is below the stated limit.

This effect consists of the lengthening of the service life of the catalyst, ie the period after which for economic reasons - because of a lack of selectivity and/or activity - regeneration of the catalyst is necessary. This lengthening of the service life is estimated at at least one year.

The selectivity *S* is in general the yield of ethylene oxide relative to the amount of ethylene which has reacted. Since the oxygen conversion rate is general held at 50% the measured selectivity is designated *S*<sub>50</sub>.

A measure of the activity *A* of the catalyst is the temperature at which with constant throughput through the reactor an oxygen conversion rate of 50% is achieved. This measure is designated *A*<sub>50</sub>.

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<sup>1</sup> Translator's note: "OS" = "Offenlegungsschrift" = published, unexamined patent application.

The production of ethylene oxide can, moreover, be carried out under any arbitrarily chosen conditions within the general conditions for the gas-phase reaction of ethylene with oxygen, ie with a gas mixture which in addition to inert gases such as methane, ethane, argon, helium and nitrogen contains 3-80 vol-% of ethylene and 2-20 vol-% of oxygen, a temperature of 200-300°C under a pressure of 1-50 bar and with a catalyst load factor of 500-15000 litres of gas mixture per hour per kilogram of catalyst. As a rule it is advisable to use 0.1-10 ppm of a halogenated hydrocarbon such as vinyl chloride in the gas mixture as well.

#### Example 1

##### Production of various catalysts

The production of each catalyst was based on 1 kg of a support material (T) consisting of sintered  $\alpha$ - $\text{Al}_2\text{O}_3$  rings 7.5 mm in diameter. This material was impregnated with a solution of 139 g of silver nitrate, 120 g of 2-butylamine, 1.4 g of lithium nitrate and 29-35 g of water, the quantity of liquid corresponding exactly to the absorptive capacity of the support material. This impregnated material was then dried for 15 mins at 220°C in the convection oven so that the silver was precipitated in metallic form on the support. The catalyst obtained in this way was then dosed with caesium by impregnating it with a solution consisting of 16.4 mg of caesium hydroxide, 0.5 g dodecylamine and 16.2 g methanol and then dried at 220°C under nitrogen.

The catalysts (K) so produced, which differed only in the silicon content of the support material, had the following composition:

ca 92 wt-%  $\alpha$ - $\text{Al}_2\text{O}_3$  as support material  
8.1 wt-% silver  
0.015 wt-% lithium (calculated as metal)  
0.015 wt-% caesium (calculated as metal)

The support materials used were:

T<sub>0</sub> (as a comparison)

- commercial material containing 110 ppm of alkali-soluble Si compounds, calculated as  $\text{SiO}_2$ ;

T<sub>1</sub> (in accordance with the invention)

- high-purity commercial material containing < 1 ppm of alkali-soluble Si compounds;

T<sub>2</sub> (in accordance with the invention)

- the support material T<sub>0</sub> was boiled for 30 mins with 1 litre of 1 wt-% sodium hydroxide solution and then washed until neutral with totally deionised water; as a result of this treatment the content of alkali-soluble Si compounds fell to below 1 ppm;

T<sub>3</sub> (in accordance with the invention)

- the support material T<sub>0</sub> was boiled for 10 mins with 1 litre of 1 wt-% hydrofluoric acid and then washed until neutral with totally deionised water; as a result of this treatment the content of alkali-soluble Si compounds fell to below 1 ppm.

#### Example 2

##### Test of catalysts under practical conditions

For the tests a sample of each of the catalysts K<sub>0</sub> - K<sub>3</sub> defined by the support materials T<sub>0</sub> - T<sub>3</sub> was size-reduced to an average particle size of 0.5 mm. 10 ml (bulk volume) of each sample was exposed for one hour in a test reactor with an internal diameter of 5 mm under a pressure of 15 bar to 30 litres (standard conditions) of a gas mixture consisting of 28 vol-% of ethylene, 8 vol-% of oxygen, 2 ppm of vinyl chloride and the rest nitrogen, the temperature being set so that 50% oxygen consumption was achieved. This temperature is a measure of the activity A<sub>50</sub>. The yield of ethylene oxide corresponding to this 50% oxygen consumption is the selectivity S<sub>50</sub>.

The results of these tests after runs lasting 2 days and two weeks are summarised in the following table.

Catalyst		Support alkali-soluble SiO <sub>2</sub> content	S <sub>50</sub> (%) after		A <sub>50</sub> (°C) after	
			2 days	2 weeks	2 days	2 weeks
K <sub>0</sub>	T <sub>0</sub>	110	81.6	80.7	219	221
K <sub>1</sub>	T <sub>1</sub>	1	81.7	81.4	218	218
K <sub>2</sub>	T <sub>2</sub>	1	81.7	81.5	218	218
K <sub>3</sub>	T <sub>3</sub>	1	81.4	81.4	219	219

It can be seen that the activity A<sub>50</sub> remained constant in the case of the catalysts in accordance with the invention while the loss of activity in the case of the reference catalyst had to be compensated for by a 2°C higher temperature.

In the case of the catalysts in accordance with the invention the selectivity S<sub>50</sub> remained constant within the analytical accuracy of  $\pm 0.2\%$ . Compared with this the decrease in the case of K<sub>0</sub> was significantly greater and permits the generalisation of a loss of selectivity of more than half a percentage point.

### Example 3

#### Model tests

The catalyst K<sub>1</sub> was modified with part of the lithium nitrate being replaced by lithium silicate so that the catalyst contained an artificial content of alkali-soluble silicon compounds. The catalysts K<sub>1'</sub> - K<sub>1'''</sub> obtained in this way were then tested as in Example 2. The table below shows graphically the adverse effect of the alkali-soluble Si compounds

Catalyst	alkali-soluble SiO <sub>2</sub> content (ppm)	S <sub>50</sub> (%) after		A <sub>50</sub> (°C) after	
		2 days	3 days	2 days	3 days
K <sub>1</sub>	1	80.6	80.6	222	222
K <sub>1'</sub>	200	80.0	79.4	222	223
K <sub>1''</sub>	600	77.6	76.5	227	233
K <sub>1'''</sub>	1000	76.3	74.5	235	247